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Volatility of In-Use Gasoline and Gasoline/Methanol Blends

Southwest Research Inst., San Antonio, TX

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Volatility of In-Use Gasoline and Gasoline/Methanol Blends

by

Charles M. Urban

Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

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EPA Project Officers: Robert J. Garbe
Craig A. Harvey
EPA Branch Technical Representative: Robert J. Garbe

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16. ABSTRACT

This report provides results of analyses for alcohol content, volatility, and other properties of forty in-use unleaded gasoline samples. Analyses conducted on these fuels included: methanol, ethanol, and tertiary butyl alcohol (TBA) quantitation; Reid vapor pressure; distillation; water and lead content; and the calculation of FEVI and EI volatility indices. Twenty-two of the forty samples contained between three and five percent methanol. Most of the gasoline samples, including those not containing methanol, contained several percent TBA. Data obtained indicated the volatility of fuels containing methanol and TBA were not significantly different from that of fuels containing only TBA. The data also showed an average RVP of 13.3 and 13.6 psi respectively for these fuels, which, is above the maximum ASTM specified RVP of 11.5 psi for the Houston area at the time these samples were taken.

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FOREWORD

This Work Assignment was initiated by the Control Technology Assessment and Characterization Branch, Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan 48105. The effort on which this report is based was accomplished by the Department of Emissions Research of Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas 78284. This program, authorized by Work Assignment 14 under Contract 68-03-3162, was initiated February 29, 1984 and was completed September 28, 1984. The program was identified within Southwest Research Institute as Project 03-7338-014.

This Work Assignment was conducted by Mr. Charles Urban, Project Leader, and Mr. Joseph Fisher, Task Leader for the fuels sampling and analyses. Mr. Charles Hare was Project Manager and was involved in the initial technical and fiscal negotiations and subsequent major program decisions. The EPA Project Officers were Mr. Robert J. Garbe and Mr. Craig A. Harvey of the Technical Support Staff, Environmental Protection Agency.

ABSTRACT

This report provides results of analyses for alcohol content, volatility, and other properties of forty in-use unleaded gasoline samples. Analyses conducted on these fuels included: methanol, ethanol, and tertiary butyl alcohol (TBA) quantitation; Reid vapor pressure; distillation; water and lead content; and the calculation of FEVI and EI volatility indices. Twenty-two of the forty samples contained between three and five percent methanol. Most of the gasoline samples, including those not containing methanol, contained several percent TBA. Data obtained indicated the volatility of fuels containing methanol and TBA were not significantly different from that of fuels containing only TBA. The data also showed an average RVP of 13.3 and 13.6 psi respectively for these fuels, which, is above the maximum ASTM specified RVP of 11.5 psi for the Houston area at the time these samples were taken.

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I. INTRODUCTION

The objective of this Work Assignment was to obtain and analyze forty samples of in-use gasoline. It was desired that about half of the samples contain Oxinol, a fuel additive containing methanol and tertiary butyl alcohol. All gasoline samples were to be obtained, in an essentially random manner, from Seven-Eleven Stores in and around Houston, Texas.

Analyses of these gasoline samples included: methanol, ethanol, and TBA content; Reid vapor pressure (RVP); distillation; and water and lead content. Distillation and RVP data were then utilized to calculate FEVI and EI volatility indices. Graphical presentation and statistical analyses, to the extent appropriate, were applied to the data to determine trends, especially as regards comparisons between the base unleaded gasolines and the gasoline/Oxinol blends.

II. GASOLINE SAMPLING

Contact was made with the Southland Corporation, provider of fuels to Seven-Eleven Stores in Houston, in an attempt to determine which stores were distributing base gasoline and which were distributing Oxinol/gasoline blends. The requirements for obtaining such information were stated to be as follows: EPA would have to write a letter of request; Southland's attorneys would review the request; and if approved, SwRI would be provided the information. The EPA Project Officer decided that time requirements did not allow for this written approach toward obtaining information. It was confirmed verbally that base gasolines and gasoline-methanol blends were being provided to the Seven-Eleven Stores. Based on a very informal sampling, the personnel at the individual stores did not appear to know whether or not the unleaded gasoline they were selling contained methanol. A decision was reached by the EPA Project Officer to initially obtain the total of 40 fuel samples in an essentially random sampling of the Seven-Eleven Stores in Houston, Texas.

The sample site selections were made on the basis of information on Seven-Eleven Stores as found in the Houston telephone directory. There were about 165 stores listed within Houston districts. Therefore, one-fourth of the stations within each district were designated for samples. Choices were made for each district by selecting the second store listed in the telephone directory, followed by each fourth store thereafter. At the request of the EPA Project Officer, duplicate fuel samples were taken at several of the stations, and those samples were sent to the EPA for analyses.

Provisions were included to allow substitutions within a district when a sample could not be obtained from a designated store (e.g., some stores were closed, some were no longer selling gasoline, etc.). The primary aim was to obtain forty fuel samples (plus several duplicate samples) in an unbiased manner from Seven-Eleven Stores in the Houston area, with the selected stores having reasonable geographic distribution. Sampling and handling procedures used are described in Appendix A.

All samples were collected during the period of late March through April. The source locations of the samples are listed in Table 1. Less than ten source substitutions were required in the original list of forty sources, and several of these substitutions were to another Seven-Eleven Store a few blocks away on the same street.

All pumps from which gasoline samples were taken were labeled with an R + M/2 octane number of 87. There was no indication on any of the pumps that the gasoline contained alcohols. With few exceptions, in subsequent analyses it was determined that gasoline samples from the south side of Houston contained methanol, and those from the north side did not contain methanol. The reason for the differing methanol content in different areas of Houston was not determined, but it was possibly due to different terminals distributing gasoline to different parts of the city.

At the direction of the Project Officer, effort allocated for large-quantity sampling was redirected toward preparation of two fuel batches for

TABLE 1. LOCATION OF SEVEN-ELEVEN STORES SAMPLED

Sample Number	District	Address
1	Southwest	6031 Willow Bend
2	Championsa	11050 S. Post Oak
3	West	6333 San Felipe
4	West	1100 W. Alabama
5	West	9230 Buffalo Spwy.
6	Northwest	6541 W. 43rd
7	North	7501 Airline
8	North	10301 Shady Lane
9	North	2331 Little York
10	Northwest	4730 Brinkman
11	Northwest	1302 N. Shepherd
12	Championsb	5623 Aldine Bender
13	Northwest	5718 W. 34th
14	Championsb	2950 Greens Road
15	Northwest	602 W. Parker Road
16	North	5711 Irvington
17	Northwest	4401 Irvington
18	West	1326 Dairy Ashford
19	North	4809 N. Main
20	North	2302 White Oak
21	Southeast	8637 Glenvista
22	South	9602 Telephone
23	Southeast	4302 Telephone
24	Northwest	2050 Bingle
25	Southeast	6154 Bellfort
26	Pasadenaa	5010 Red Bluff
27	Pasadenaa	2521 Strawberry
28	Pasadenaa	902 Allen Genoa Road
29	Pasadenaa	3500 Fairmont Pkwy
30	Pasadenaa	6402 Spencer
31	South	10855 Telephone
32	Pasadenaa	901 W. Harris
33	Pasadenaa	502 S. Shaver
34	Pasadenaa	3202 Pasadena Frwy
35	South	11402 Hughes
36	Southwest	8920 Bissonnet
37	Southwest	11313 Fondren
38	West	5805 Bellair
39	South	10602 Fugua
40	Southwest	10096 S. Gessner

[a]Southeast side of Houston
[b]North side of Houston

use at EPA's Ann Arbor facility. These fuels were an 11.0-11.5 RVP commercial base gasoline, and a blend of the heavier ends of this gasoline with 9.5% Oxinol to achieve a fuel with a matching Evaporative Index. The effort was started under Work Assignment No. 1 of Contract 68-03-3192 and concluded under the subject assignment. A description of the fuel treatment and blending processes is included as Appendix A-5 to this report. All fuel drums of each fuel were shipped to EPA.

III. ANALYTICAL PROCEDURES

The analytical procedures and calculations used in evaluating the gasoline samples are as follows:

- REID VAPOR PRESSURE (RVP) - Automatic RVP Instrument Method. It has been determined by the ASTM that the conventional "wet-bomb" method (ASTM D-323) is not satisfactory for analysis of gasoline-alcohol blends. The Automatic RVP Instrument, developed at SwRI and used to analyze all MVMA survey samples, has been found to be a satisfactory alternate method. This method is described in Appendix B.

- DISTILLATION - ASTM D-86.

- METHANOL, ETHANOL, AND TERTIARY BUTYL ALCOHOL (Volume Percent) - Water Extraction/Gas Chromatography. There are currently no standard ASTM Procedures for determination of alcohols in gasoline. SwRI has developed a reliable analytical procedure based on extraction of the gasoline with 2 volumes of water and gas chromatography of the extract using a flame ionization detector. Full details are given in Appendix B. This method is used to analyze MVMA survey samples.

- WATER (Weight Percent) - ASTM D-1744, Karl Fischer Titration (pyridine free).

- LEAD (Weight Percent) - ASTM D-3237, Atomic Absorption Spectrometry.

- FEVI AND EI VOLATILITY INDICES - These indices were calculated from the RVP and distillation data using formulas supplied by EPA:

  FEVI = RVP + 0.13x(% EVAP @ 158°F)

  EI = 1.1xRVP - 0.32x(% EVAP @ 100°F) + 0.21x(% EVAP @ 200°F

The distillation, water content, and lead content evaluations involve standard ASTM methods for which repeatabilities have been established, although it is not known if these repeatabilities are directly applicable to gasoline/methanol blends:

- Distillation D-86 - Repeatability varies from about 2 to 5°F depending on the rate of temperature rise.

- Water Content D-1774 - Repeatability applicable to aviation turbine fuels is about 0.001 percent for water content between 0.005 and 0.1 percent.

- Lead Content D-3237 - Repeatability is 0.005 g/gal.

For the alcohol content and the RVP evaluations, a control sample was analyzed periodically . Five individual gallon samples of a single batch of fuel containing Oxinol were analyzed for alcohol content and RVP; one at the start of the analysis of the in-use gasoline samples, and one each tenth sample thereafter. Although of value here only for purposes of comparison, the repeatability and reproducibility for the standard ASTM D 323 RVP method are 0.25 and 0.55 psi respectively within the range of 0 to 15 psi.

IV. RESULTS OF THE GASOLINE ANALYSES

Results of the analyses on the forty gasoline samples are summarized in Tables 2 and 3, and details concerning the EI and FEVI volatility index calculations are given in Appendix C. Relationships between parameters are discussed in Section V of this report. The following discussion is based on the data in Table 2.

RVP - The RVPs ranged from 12.4 to 14.3 psi for the samples that contained methanol (MeOH), and from 13.3 to 14.3 psi for those not containing methanol. The average RVPs were 13.3 and 13.6 psi, respectively. For the control samples, the RVP results were as follows:

Analyses	RVP, psi
Initial	10.3
Between Samples 10&11	10.2
Between Samples 20&21	10.2
Between Samples 30&31	10.2
Final	10.1

According to ASTM D 439 the specified seasonal RVPs for the Houston area are:

Month	Volatility Designation	Max. RVP, psi
January	D	13.5
February	C	11.5
March	C	11.5
April	C or B	11.5
May	B	10.0
June	B	10.0
July	B	10.0

The forty fuel samples analyzed in the work assignment were all collected during the period of late March through April.

RVP analyses of four duplicate samples (Numbers 23, 34, 35, 37) were performed by the EPA, and the results obtained were reported to be 0.4 to 0.7 psi lower than the values obtained under this Work Assignment. These values obtained by the EPA support those determined by SwRI within reasonable limits for the four samples, and by extrapolation do so for all forty samples.

Alcohol Content - With one exception, the gasoline samples either contained 4.5 to 4.9 percent by volume methanol, or no methanol. In general, samples from the south side of Houston contained methanol, and those from the north side did not contain methanol. No ethanol was detected in any of the forty samples. Samples containing 4.5 to 4.9 percent methanol were found to

TABLE 2. SUMMARY RESULTS OF FUELS ANALYSES

Sample Number	District	% by Volume MeOH	% by Volume TBA	RVP, psi	Water Content Percent	Lead, g/gal	Distillation, °F at % Evap. 10%	50%	90%	Calculations EI	FEVI
1	Southwest	4.9	4.3	14.2	0.10	0.002	102	189	333	23.8	19.4
2	Champions	4.6	4.2	14.3	0.12	0.001	103	195	340	23.7	19.4
3	West	4.6	4.1	14.1	0.11	0.002	107	203	345	22.5	18.9
4	West	0	0.3	13.5	0.02	0.001	97	188	338	22.3	18.7
5	West	0	0.2	13.5	0.01	0.001	95	198	345	21.4	18.4
6	Northwest	0	3.9	13.6	0.10	0.002	101	183	339	23.4	18.9
7	North	0	7.0	13.3	0.19	0.004	99	173	348	23.3	18.9
8	North	0	4.8	14.1	0.13	0.001	100	186	347	23.6	19.3
9	North	0	6.9	13.5	0.19	0.003	102	181	348	23.4	18.8
10	Northwest	0	3.9	14.0	0.09	0.002	98	173	335	24.0	19.7
11	Northwest	0	4.6	13.6	0.12	0.001	101	185	348	23.2	18.9
12	Champions	0	6.8	13.5	0.21	0.001	106	185	352	23.6	18.4
13	Northwest	0	5.9	14.3	0.18	0.002	98	168	338	24.6	19.4
14	Champions	0	7.0	13.4	0.20	0.001	102	179	348	23.5	18.7
15	Northwest	0	5.8	13.8	0.20	0.001	101	185	347	23.4	18.9
16	North	0	5.8	13.4	0.19	0.003	104	178	347	23.8	18.9
17	Northwest	0	5.3	13.5	0.17	0.001	104	179	357	23.8	18.9
18	West	0	1.1	13.9	0.02	0.003	96	187	331	24.2	19.3
19	North	0	0.8	13.8	0.01	0.001	92	193	341	23.1	19.0
20	North	0	6.1	13.4	0.18	0.025	103	173	348	24.0	19.0
21	Southeast	4.6	4.0	13.2	0.12	0.001	106	193	336	23.1	18.2
22	South	4.5	4.2	13.7	0.12	0.001	108	196	340	23.7	18.7
23	Southeast	4.7	4.2	13.7	0.11	0.001	108	195	337	23.7	18.6
24	Northwest	0	6.1	13.4	0.16	0.002	103	184	345	23.3	18.6
25	Southwest	4.7	4.2	12.9	0.11	0.004	111	202	342	22.7	17.6
26	Pasadena	4.6	4.0	13.1	0.11	0.003	110	202	332	22.9	17.8
27	Pasadena	4.7	4.2	13.1	0.11	0.002	108	195	339	23.1	18.1
28	Pasadena	4.5	4.0	12.7	0.18	0.002	114	207	339	22.9	17.2
29	Pasadena	4.7	4.2	13.1	0.11	0.001	109	197	345	23.2	18.0
30	Pasadena	4.5	4.0	12.7	0.11	0.001	108	204	339	22.4	17.4
31	South	4.9	4.4	13.1	0.11	0.001	110	199	343	23.2	18.0
32	Pasadena	3.3	2.9	13.1	0.09	0.001	103	195	341	22.5	18.0
33	Pasadena	4.6	4.1	13.2	0.12	0.001	107	198	341	23.0	18.2
34	Pasadena	4.7	4.1	13.1	0.14	0.001	102	194	333	22.4	18.1
35	South	4.7	4.1	12.4	0.12	0.002	104	196	332	21.7	17.3
36	Southwest	4.7	4.2	14.3	0.11	0.002	105	195	345	23.9	19.3
37	Southwest	4.7	4.1	12.9	0.11	0.002	109	200	341	22.8	17.7
38	West	4.6	4.1	12.9	0.11	0.004	107	202	332	22.4	17.6
39	South	4.5	4.0	13.1	0.11	0.002	109	199	335	22.9	17.9
40	Southwest	4.8	4.3	13.8	0.11	0.001	105	187	349	23.9	19.1
Avg. with MeOH		4.7	4.1	13.3	0.12	0.002	107	198	339	23.1	18.2
Avg. w/o MeOH[a]		0	5.7	13.6	0.17	0.002	101	179	346	23.6	19.0
Avg. w/o MeOH		0	0.6	13.7	0.02	0.002	95	192	339	22.8	18.9
S.D. with MeOH		0.1	0.1	0.6	0.02	0.001	3	5	5	0.7	0.7
S.D. w/o MeOH[a]		0	1.1	0.3	0.04	0.001	2	6	6	0.4	0.3

[a]Excluding sample numbers 4, 5, 18, and 19

TABLE 3. DISTILLATION DATA

Sample Number	Pct. MeOH	Temperature °F at % Evaporated													
		IBP	5%	10%	15%	20%	30%	40%	50%	60%	70%	80%	90%	95%	EP
1	4.9	78	86	102	110	116	132	157	189	222	252	286	333	365	395
2	4.6	81	89	103	111	118	134	160	195	233	265	299	340	374	415
3	4.6	85	91	107	115	122	139	167	203	238	270	302	345	375	414
4	0	75	85	97	106	114	133	158	188	222	255	293	338	372	403
5	0	72	81	95	104	113	136	164	198	234	271	307	345	375	413
6	0	79	88	101	110	118	135	155	183	218	253	295	339	372	409
7	0	78	87	99	106	118	136	152	173	209	253	304	348	379	403
8	0	80	86	100	111	119	137	158	186	223	261	302	347	380	415
9	0	76	88	102	111	121	140	157	181	218	260	307	348	379	412
10	0	80	87	98	107	115	130	149	173	207	243	286	335	366	397
11	0	77	87	101	110	118	135	156	185	222	261	303	348	381	414
12	0	82	90	106	116	126	144	162	185	225	270	312	352	384	423
13	0	76	87	98	106	115	131	148	168	202	231	285	338	374	403
14	0	80	90	102	112	122	139	156	179	217	261	305	348	381	405
15	0	81	86	101	111	121	139	159	185	222	262	305	347	377	413
16	0	80	91	104	113	120	137	153	178	214	259	304	347	374	413
17	0	90	91	104	113	121	137	154	179	216	260	306	357	384	416
18	0	77	85	96	104	112	129	154	187	221	253	286	331	367	395
19	0	74	81	92	101	109	129	159	193	226	259	294	341	376	408
20	0	81	91	103	112	120	136	151	173	208	256	305	348	381	409
21	4.6	87	95	106	114	120	135	163	193	230	261	295	336	376	412
22	4.5	87	97	108	115	122	136	161	196	235	269	304	340	377	416
23	4.7	84	95	108	116	123	139	163	195	230	262	298	337	376	416
24	0	81	91	103	113	122	139	158	184	223	264	302	345	376	412
25	4.7	86	98	111	119	126	142	169	202	236	268	300	342	376	409
26	4.6	84	98	110	117	124	140	169	202	232	258	288	332	373	416
27	4.7	84	96	108	116	122	137	162	195	229	260	296	339	368	412
28	4.5	91	104	114	120	127	143	174	207	238	264	296	339	375	416
29	4.7	86	98	109	116	122	137	164	197	228	255	290	345	384	415
30	4.5	86	99	108	115	123	140	169	204	234	261	291	339	375	408
31	4.9	86	99	110	117	123	138	165	199	231	262	295	343	379	410
32	3.3	80	91	103	110	117	137	164	195	225	254	293	341	376	413
33	4.6	83	96	107	113	121	137	163	198	230	259	290	341	383	418
34	4.7	84	91	102	111	118	135	161	194	225	252	284	333	372	412
35	4.7	85	90	104	112	119	137	164	196	228	256	287	332	363	400
36	4.7	79	92	105	114	121	137	162	195	232	266	303	345	380	411
37	4.7	87	98	109	116	123	139	167	200	232	263	295	341	372	404
38	4.6	88	96	107	116	124	141	169	202	235	265	296	332	370	408
39	4.5	84	96	109	116	123	139	166	199	228	251	283	335	377	415
40	4.8	81	93	105	112	118	132	156	187	227	266	305	349	386	415
Avg.	4.7	85	95	107	115	122	138	164	198	231	261	294	339	375	411
Avg.[a]	0	79	88	101	111	120	137	155	179	215	256	301	346	378	410
Avg.	0	75	83	95	104	112	132	159	192	226	260	295	339	373	405
S.D.	4.7	3	4	3	3	3	3	4	5	4	6	7	5	6	6
S.D.[a]	0	2	2	2	3	3	4	4	6	7	10	8	6	5	7

[a]Excluding sample numbers 4, 5, 18, and 19

also contain 4.0 to 4.4 percent TBA (an average of 87 percent as much TBA as methanol). One sample (Number 32) contained 3.3 percent methanol and 2.9 percent TBA (88 percent as much TBA as methanol). For the control samples, no ethanol was detected, and the methanol (MeOH) and TBA concentrations were as follows:

Analyses	Volume Percent MeOH	TBA
Initial	4.8	4.5
Between Samples 10&11	4.4	4.1
Between Samples 20&21	4.5	4.2
Between Samples 30&31	4.5	4.1
Final	4.6	4.2

All forty in-use samples contained measurable amounts of TBA. Ten samples, out of the eighteen with no measurable methanol, contained over five percent TBA. Only three samples contained less than one percent TBA, and only five samples had less than three percent TBA.

Water Content - The average water content was 0.12 weight percent for the samples containing methanol, 0.17 percent for the samples without methanol that contained over 1.1 percent TBA, and 0.02 percent for the samples without methanol that contained 1.1 percent TBA or less. The ranges of the water content were 0.09 to 0.18, 0.10 to 0.21, and 0.01 to 0.02 percent, respectively. For the samples that did not contain methanol, there appeared to be some relationship between TBA content and the water content.

Lead Content - With the exception of one sample (Number 20) having a lead content of 0.025 g/gal, the lead content ranged from 0.001 to 0.004 g/gal. With the method of analyses having a repeatability of 0.005 g/gal, only the 0.025 g/gal result appears to represent a significant value.

Distillation - Excluding the four samples having less than 1.2 percent TBA, the methanol-containing samples required higher temperatures for 10% and 50% distillation and a lower temperature for 90% distillation. Detailed distillation data are given in Appendix C. For all samples distilled, the residue was one percent and the losses ranged from one to three percent. The average losses were 2.0 percent for the samples containing methanol, and 2.4 percent for the samples with no measurable methanol.

EI and FEVI Volatility Indices - The EI varied from 21.7 to 23.8, with an average of 23.1, for the samples containing methanol; and from 21.4 to 24.6, with an average of 23.4, for the samples having no measurable methanol. The FEVI varied from 17.2 to 19.4, with an average of 18.2, for the samples with methanol; and from 18.4 to 19.4, with an average of 19.0, for the samples with no methanol.

V. ANALYSIS AND DISCUSSION OF THE DATA

The data obtained were analyzed for trends, especially as regards comparisons between the samples without methanol and the Oxinol/gasoline blends. Initial analyses involved plotting of various parameters; several of these plots are given in Figures 1 through 5.

With reference to Figures 1 and 2, there is no observable relationship between the RVP and the methanol concentration, or between the RVP and the TBA concentration. With reference to Figure 3, there is some difference between the average distillation curves for samples with and without methanol, the maximum difference being a temperature of 11°C(19°F) at fifty percent evaporated. With reference to Figure 4, there is an apparent relationship between the EI and the FEVI volatility indices. With reference to Figure 5, there appears to be some relationship between water content and the concentration of TBA. The available data, however, do not enable specific determination of that relationship with a reasonable degree of confidence. Based on observations of the plotted data, detailed statistical analyses were considered inappropriate.

There are several observations and conclusions, however, which can be made concerning the data generated on the forty gasoline samples:

1. Of the 22 samples containing methanol, 21 had methanol concentrations between 4.5 and 4.9 percent. On the average, these samples contained about 87 percent as much TBA as methanol. One methanol-containing sample had 3.3 percent methanol and 2.9 percent TBA (88 percent as much TBA as methanol). Therefore, it appears that this sample with 3.3 percent methanol may represent a blend of a base unleaded gasoline and a standard blend of Oxinol/gasoline.

2. All forty samples, including those without measurable methanol, contained tertiary butyl alcohol (TBA). Of the 18 samples having no methanol, 14 had TBA concentrations between 3.9 and 7.0 percent (with an average of 5.7 percent). The other four samples with no methanol had TBA concentrations between 0.2 and 1.1 percent (with an average of 0.6 percent).

3. None of the samples contained a measurable amount of ethanol.

4. In general, samples obtained from the south side districts of Houston contained methanol, and those obtained from the north side districts did not contain methanol. Three of the four samples containing less than 1.2 percent TBA were obtained from the west Houston district.

5. There was no observable relationship between RVP and the concentration of methanol or TBA. Average RVP for samples containing methanol was 13.3 psi, and that for samples not containing methanol was 13.6 psi. It appears likely that all samples were blended to a nominal RVP of 13.5 psi.

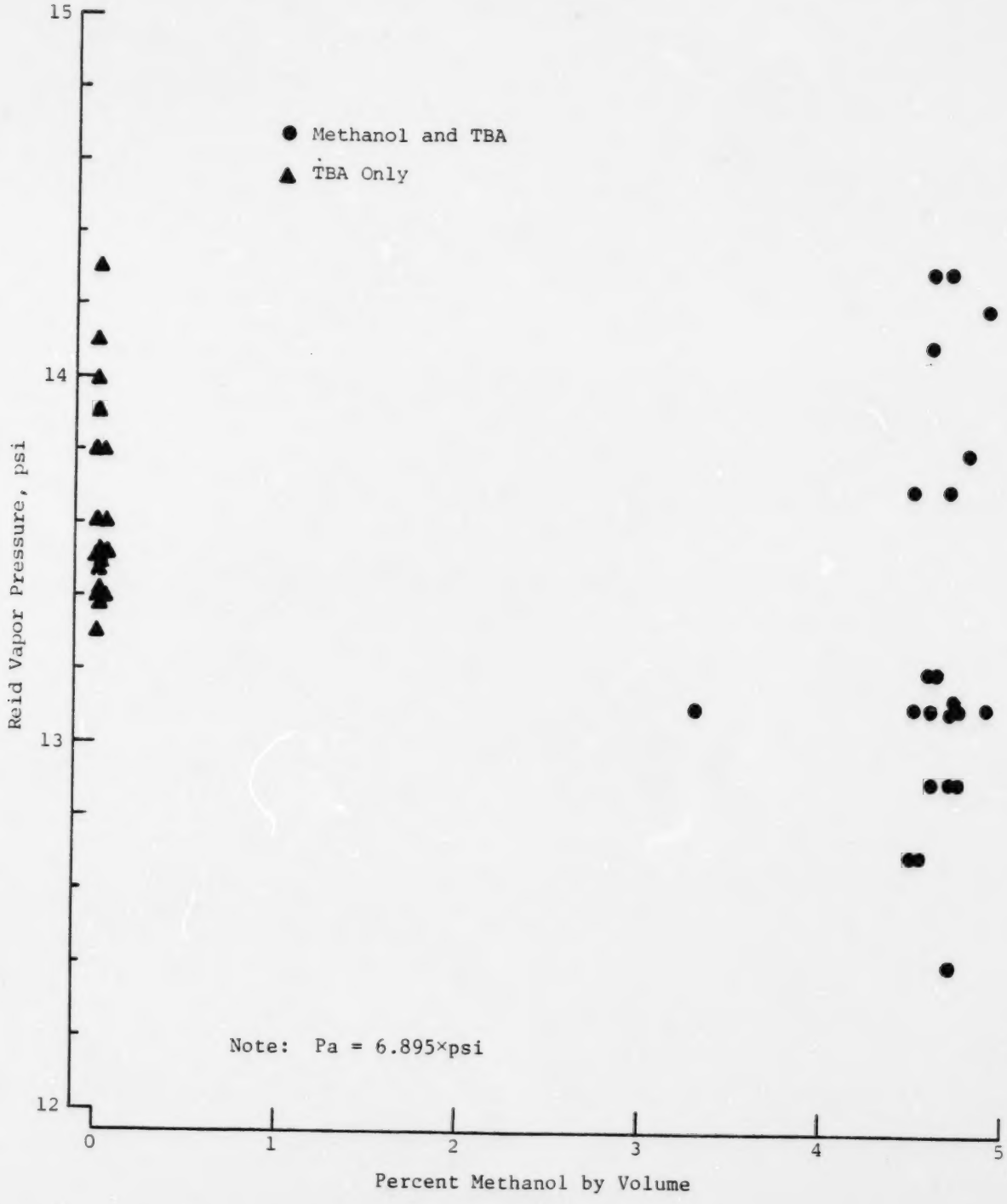

Figure 1. Relationship of RVP to methanol concentration

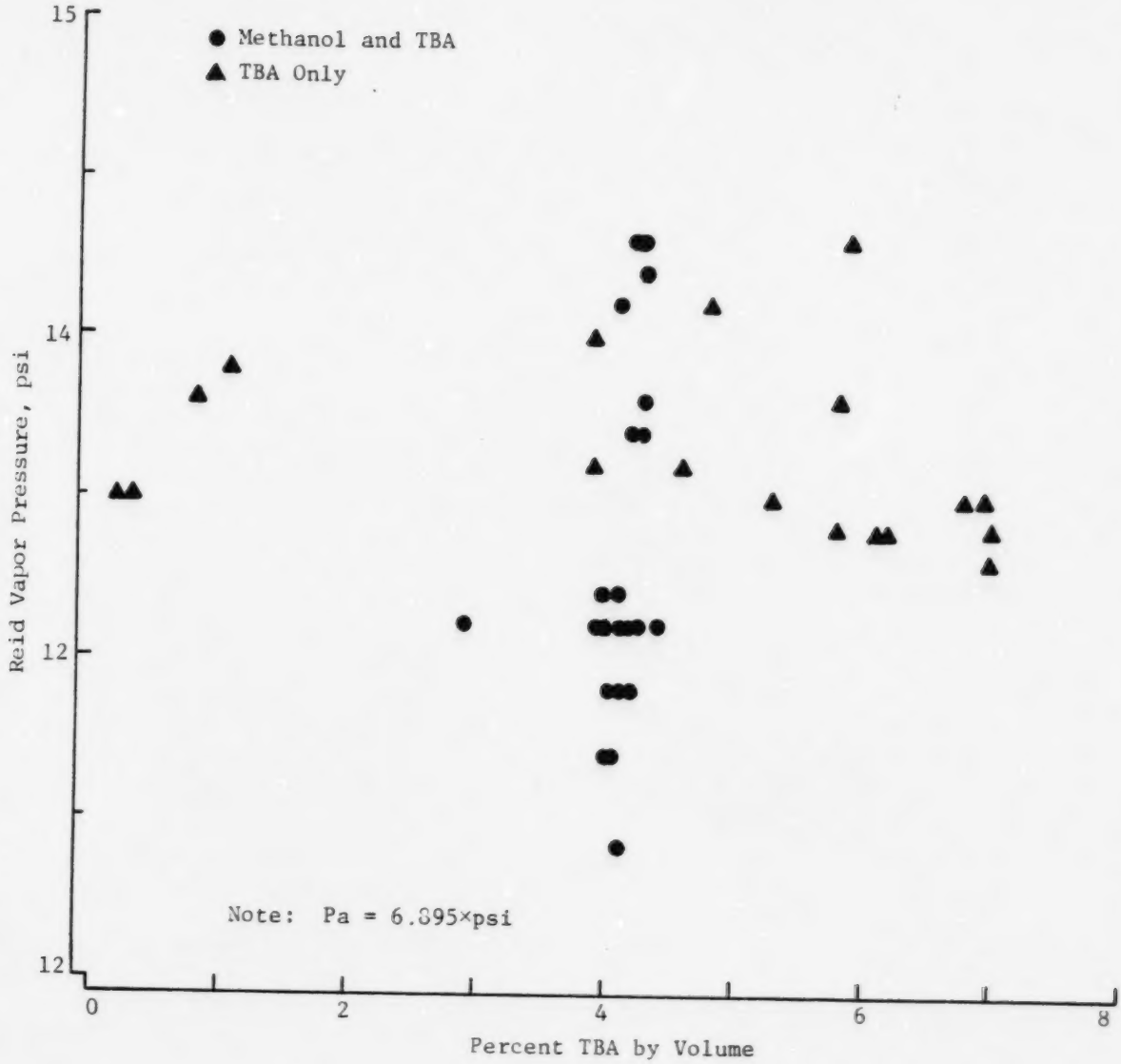

Figure 2. Relationship of RVP to TBA concentration

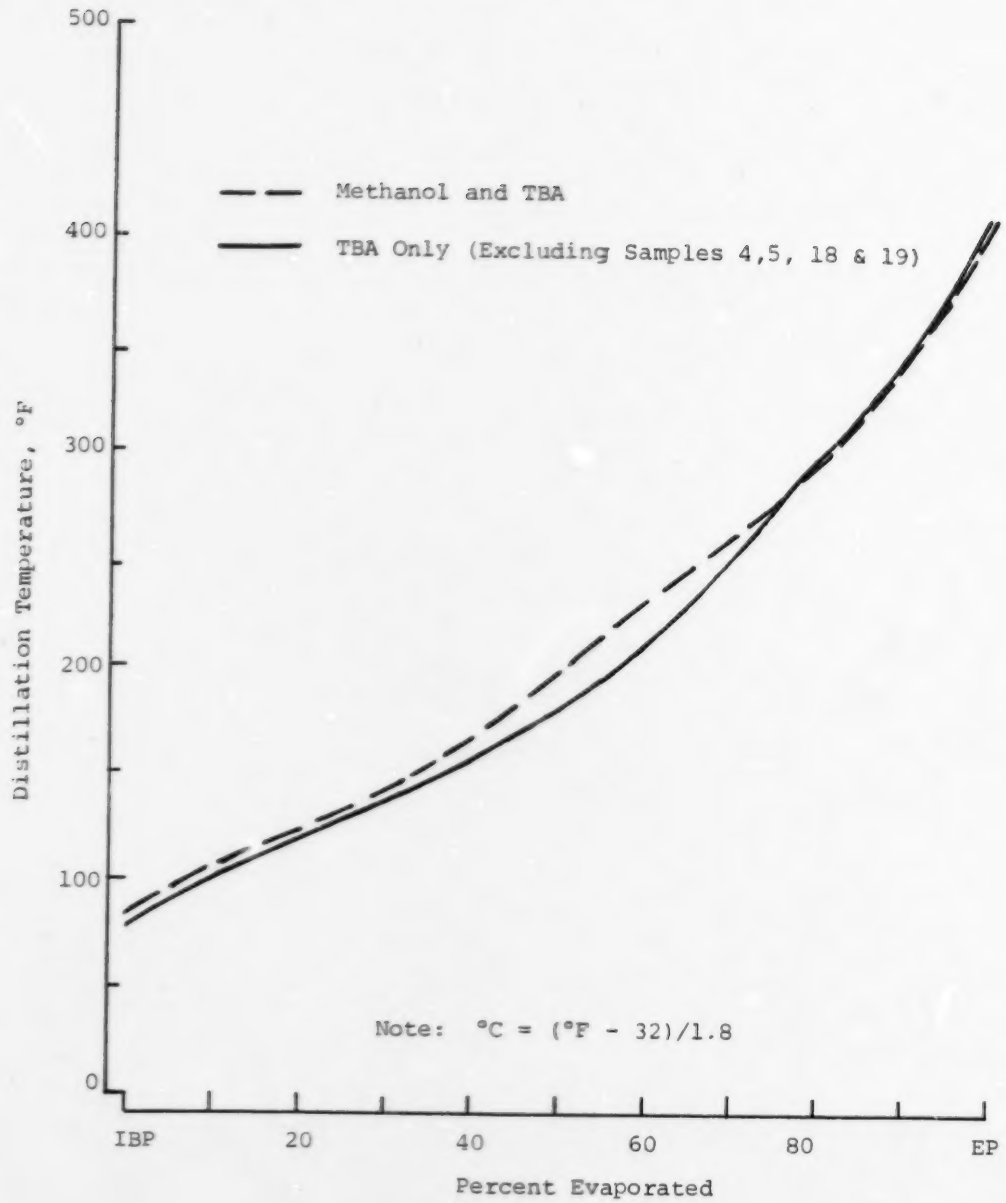

Figure 3. Plot of the average distillation values for methanol- and non-methanol-containing samples

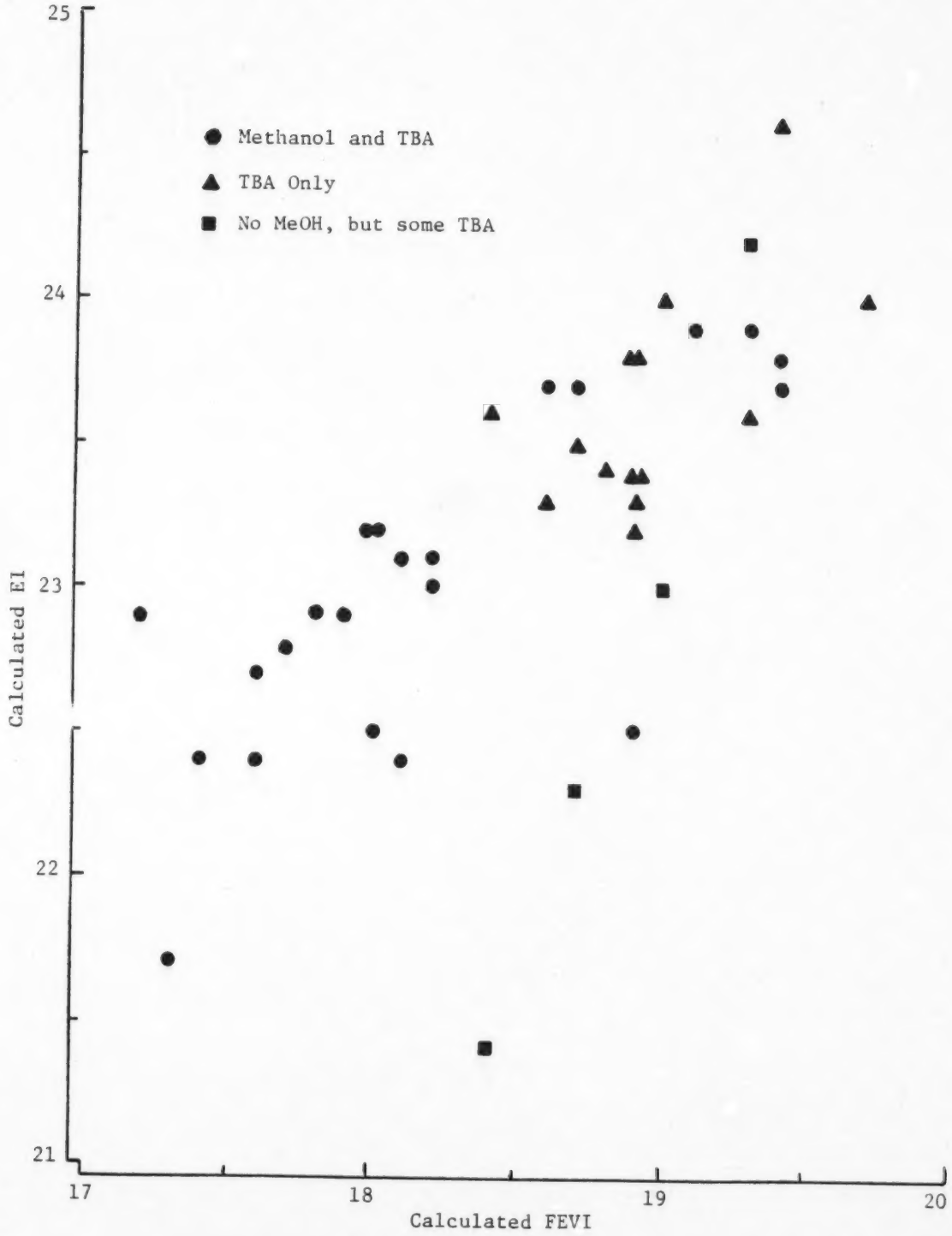

Figure 4. Relationship between EI and FEVI

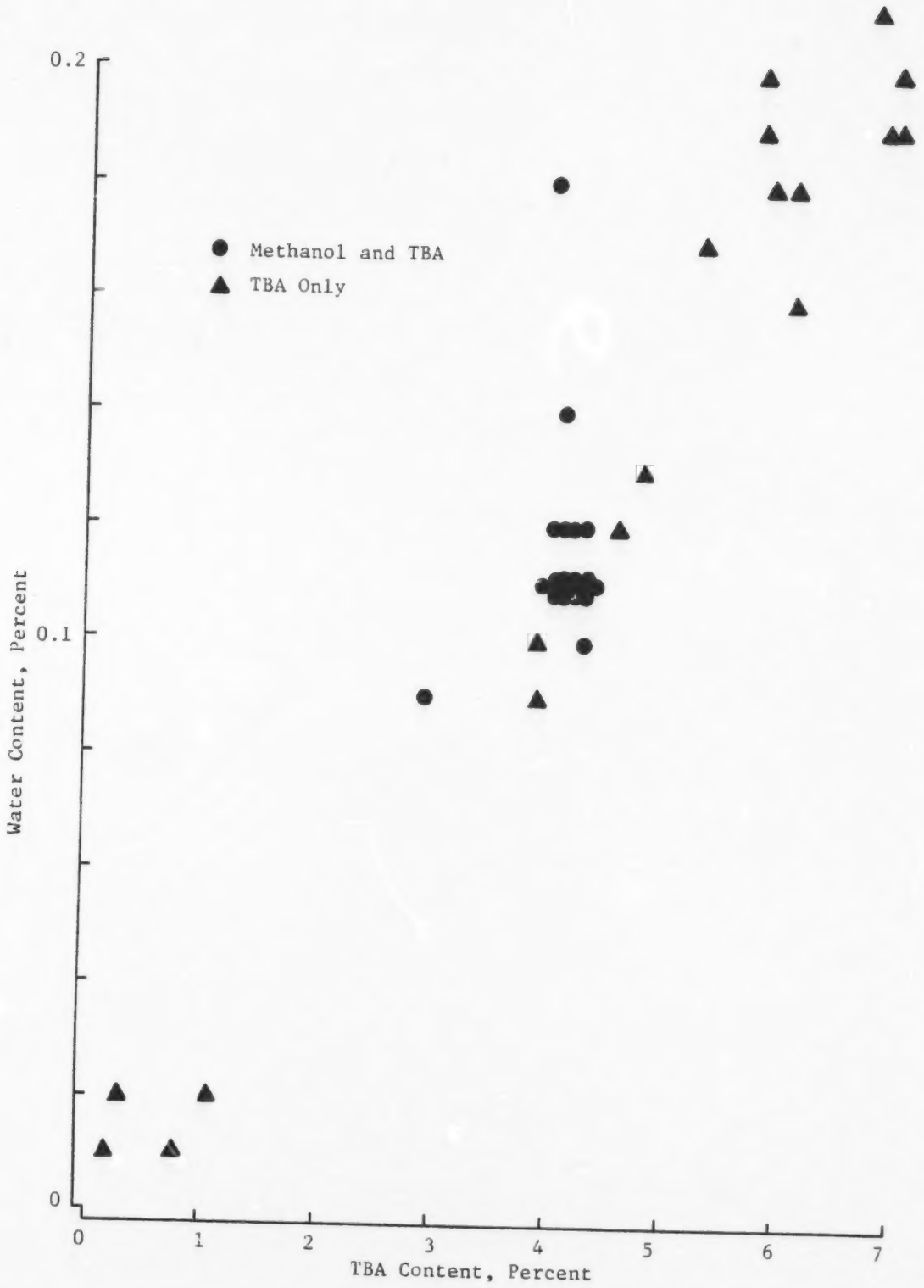

Figure 5. Relationship between water content and TBA content

6. The samples were collected during the period of late March through April.

7. There appears to be some relationship between water content and TBA concentration. Highest concentration of water in any of the samples was 0.20 percent.

8. With the exception of one sample (Number 20), the lead content was essentially negligible (i.e., it was less than the repeatability of the procedure). Sample 20 had a lead content of 0.025 g/gal, indicating some, although not excessive, contamination of that sample with leaded fuel.

9. In general, the distillation curves for samples containing methanol differed from the curves for samples containing no methanol, around mid range of the distillation. That is, the average temperature for 50 percent evaporated was 198°F for the samples containing methanol, and 179°F for the samples containing no methanol and over 1.1 percent TBA.

10. There were no major differences in the overall average EI or FEVI volatility indices between samples containing methanol and those containing no methanol. This result could be expected, since the volatility indices are primarily a function of the RVP, and the RVP's did not differ by any significant amount. For these samples, the RVP accounted for about two-thirds of the total value of the volatility index. There appeared to be some relationship between EI and FEVI; this could also be expected since both indices are primarily a function of the same parameter, RVP.

APPENDICES

A. MVMA SAMPLE COLLECTION PROCEDURE (MODIFIED)
B. ANALYTICAL PROCEDURES
C. CALCULATION OF VOLATILITY INDICES

APPENDIX A

MVMA SAMPLE COLLECTION PROCEDURE (MODIFIED)

A-1 GENERAL INSTRUCTIONS
A-2 DRIVER'S INSTRUCTIONS
A-3 PURCHASE-PACK-SHIP SERVICE
A-4 SAMPLE OF ORIGIN REPORT
A-5 PREPARATION OF FUELS FOR EPA

APPENDIX A-1
GENERAL INSTRUCTIONS

A package is sent to the agent two weeks prior to the pick-up date. This package contains:

a. Attachment Sheets - A list of the gasoline stations and grade of fuel to be purchased. *No substitutions are made by the agent, without the consent of Southwest Research Institute.

b. Field Origin Report - Report of the brand and location of each marketer sampled. These reports are to be completed and returned in order to be paid.

c. NA & UN Labels - Shipping regulations require these stickers to be affixed on the top of the boxes for the return shipment.

d. Letter of Instructions - enclosed.

e. Return Address Envelope - 6 1/2 x 9 1/2 Manila Envelope. This is a convenience for the agent to return the field origin reports needed.

Preparations

Tags: Each can is tagged for sample identification indicating the brand name and grade of fuel to be purchased.

Boxes: A Federal law states that all flammable liquids are to be cargo with the inscription DOT 12B APP stamped on the side of the box. These boxes are purchased thru Southwest Research Institute from Mission City, San Antonio, Texas.

Packing: Place the tagged cans into the shipping cartons with six cans to each carton. Extra cans are added if for any reason some are damaged during shipment. A shipment package is included which contains:

a. Seals - to eliminate any leaks.

b. Caution stickers - prevent any danger during shipment.

c. Return address - Address to the Department of Petroleum Chemistry Laboratory

d. SwRI tape - To seal the boxes before shipping to Southwest Research Institute

APPENDIX A-2
DRIVER'S INSTRUCTIONS

Making the Purchase

1. Insert the nozzle of the hose near the bottom of the can.

2. Fill the cans with designated grade of fuel as indicated on the tag.

3. Place the seal in the opening, press down firmly, and screw the cap on hand tight.

4. Lay the can on its side and check for leaks. If the can leaks, check that the seal is snapped into place and tighten the cap sufficiently so that the can does not leak. Extra cans will be supplied so that, if a leak develops which cannot be corrected, a new sample may be taken.

Packing and Shipping

1. Affix the address and NA or UN labels to the top of shipping cartons.

   a. UN 1203 labels are to be affixed on top of shipping cartons containing gasoline samples.

   b. NA 1993 labels are to be affixed on top of shipping cartons containing diesel samples.

2. Affix the caution labels on the side of the shipping cartons.

3. Check cans once again to be certain that they will not leak in shipment. Check that the tag is secure on the can.

4. Use Attachment A as a check list to assure that all the designated fuel samples have been obtained.

5. Insert can in shipping carton with six cans to each carton. Place an empty can and/or filler in any empty space in the carton. Do not ship partially filled cartons. There must be 6 cans in each carton shipped. If there is any reason for not being able to ship samples by the deadline date on the Attachment A letter, please notify Patsy R. Perez, collect, immediately at (512) 684-5111, ext. 2868.

6. Seal the cartons with tape. Take cartons to the specified motor or air freight terminal and ship collect.

APPENDIX A-3
PURCHASE-PACK-SHIP SERVICE
FOR SOUTHWEST RESEARCH INSTITUTE
GENERAL INSTRUCTIONS

1. All supplies necessary for purchasing, packing and shipping of fuel will be furnished by Southwest Research Institute. Prior to the specified date for purchasing fuel, the following materials will be shipped to you:

   a. A sufficient number of empty cans for obtaining samples.

   b. Sample identification tags attached to each can indicating the brand name and grade of fuel to be purchased.

   c. One or more shipping cartons each accommodating six cans.

   d. Caution labels to be affixed to the top of shipping cartons.

   e. Labels addressed to Southwest Research Institute for return shipment.

   f. UN and NA labels to be affixed to the top of shipping cartons.

   g. Tape for resealing cartons for return shipment.

2. Enclosed with these instructions are the following items:

   a. Drivers instructions - instructions for the proper method of sampling and packing the fuel.

   b. Attachment A - A check list of the marketers and grades of fuel to be purchased. The sampling date is indicated here.

   c. Attachment B - A list of marketers and grades of fuel which is to be returned with the samples.

   d. Field origin report - A report of the brand and location of each marketer sampled. These reports must be completed and returned in order to be paid for the sample pick-up.

3. Important - Make every effort to obtain each sample listed.

   If there is any sample on the list that is not available, call Patsy R. Perez, collect, (512/684-5111, ext. 2868), for further instructions. Do not make any deletions or substitutions to the list without approval from Southwest Research Institute.

4. If any questions arise, please call collect; Patsy R. Perez, Southwest Research Institute, (512/684-5111, ext. 2868).

APPENDIX A-4

SAMPLE OF ORIGIN REPORT (Original and 3 Copies)

MVMA
FIELD SAMPLE
ORIGIN REPORT
SOUTHWEST RESEARCH INSTITUTE

FOR LABORATORY USE ONLY
Samples Received
Reports Received

Date Sampled

City Sampled

Brand Name

Name of Service Station

Street Address of Service Station

CHECK PROPER BOX

___ R + M/2 (S) ☐ Premium Unleaded	___ R + M/2 (U) ☐ Regular Unleaded	___ R + M/2 (G) ☐ Gasohol
Grade Name	Grade Name	Grade Name
___ R + M/2 (P) ☐ Premium Leaded	___ R + M/2 (R) ☐ Regular Leaded	
Grade Name	Grade Name	

Number of Stations of This Brand Visited to Obtain These Samples

☐ One ☐ Two ☐ Three

Remarks:

PLEASE MAIL IN DUPLICATE TO SOUTHWEST RESEARCH INSTITUTE

Retain gold copy for your records.

APPENDIX A-5
PREPARATION OF FUELS FOR EPA

MEMORANDUM

DATE: 28 March 1984
TO: C.T. Hare
FROM: J.A. Russell
SUBJECT: EPA OXINOL BLENDING CHRONOLOGY (03-7338-014)

The objective of this job has been to generate approximately 450 gallons each of (a) a base unleaded gasoline having an RVP of 11.0-11.5, and (b) a blend of the base gasoline with oxinol with both base and blend fuels having matched Dupont evaporative index:

$$EI = 1.1\ (RVP) - 0.32(\%\ EVAP\ @\ 100^{o}F) + 0.21\ (\%\ EVAP\ @\ 200^{o}F)$$

Oxinol 50 (50% methanol, 50% TBA) was obtained from John Tosh's Contra Costa County fleet for this purpose. The base gasoline was obtained from Division 08 Tank "L" and originally tested at 12.1 RVP. Since this was in excess of EPA requirements, it was necessary to nitrogen-strip the light ends from this gasoline in a clean 500-gallon tank behind Bldg. 63. Five cylinders of nitrogen were required to reduce the RVP of the base gasoline to 11.4. Since each cylinder contains 255 cubic feet of nitrogen at stp and it took roughly two hours per tank, flow rate for all nitrogen-stripping is estimated at 125 cubic feet per hour. Calculated evaporative index for the base gasoline was 21.75.

The base gasoline was then transferred to nine new 55-gallon drums and picked up by emissions lab personnel for storage. Approximately 450 gallon (actually slightly less), of tank "L" gasoline was then transferred to the 500-gallon tank and nitrogen-stripped for eight hours (four tanks), resulting in an RVP of 10.3 and an evaporative index of 20.68. One liter samples having 9.5 and 9.0 percent volume oxinol were also checked. These resulted in an RVP of 12.3 (evap. index 24.43) and 12.2 (evap. index 24.11), respectively. This was obviously too high, so the base gasoline was further stripped for four hours, resulting in an RVP 9.1 and an EI of 19.49. A one liter sample having 9.5 percent oxinol was prepared and tested out at RVP of 11.4 and and evap. index of 21.64.

This seemed adequate, so the 500-gallon tank was "dip sticked" at 383 gallons. To blend in 9.5 volume percent oxinol, I set up the equation:

$$\frac{(383)}{383 + x} \times 100 = 90.5$$

$$X = 40.2 \text{ gallons}$$

383.0 gasoline
+40.2 oxinol
423.2 gallons blend fuel

After full-scale blending, a sample was sent to the Division 08 lab and tested out at 11.5 RVP and 23.16 evap. index. After four more hours of nitrogen-stripping the RVP was down to 11.1 and the evap. index 22.42. The difference of 0.67 was considered still too high by Bob Garbe and so we stripped for two more hours (one tank, nine tank total) resulting in a final RVP of 10.7 and Evap. Index of 22.01 (difference of 0.26). This blend was drummed on March 19th as follows:

Drums 1-4: 53 gallons
Drums 5-8: equal volumes (~49 gal)
Drum 9:15 gallons

The drums were labeled Oxinol Gasoline Blend and Drum 9 also labeled "retain". It was understood that Bob Garbe wanted the first four drums shipped first with the next four at some future date. (ERL to retain 15 gallons of both base and blend).

One quart of the base gasoline and one quart of the blend were sent to Ken Jones at AFLRL for GC check of the total oxinol content. This turned out to be 8.3%, 3.9% MeoH and 4.4% TBA (47/53 ratio). A subsequent GC check on neat oxinol showed a 49/51 ratio.

Bob Garbe had one further requirement. He wanted three special sub-blends made up and RVP, Evap. Index measured for each. These were:

Blend No.	Blend/Base	RVP	Evap. Index
1	25%/75%	10.9	21.98
2	50%/50%	11.6	22.05
3.	75%/25%	11.7	21.89

Evap. Index does "peak" at 50/50 but, in my opinion, there is no difference within overall measurement/calculation error.

DISTILLATION OF SAMPLES BLENDED FOR EPA

Percent Recovered	Distillation Temperature, °F	
	Base Gasoline	Blended Gasoline
IBP	82	87
5	101	100
10	111	107
15	119	113
20	127	119
30	144	132
40	165	152
50	194	177
60	229	215
70	273	260
80	315	303
90	343	333
95	367	353
EP	395	382

APPENDIX B

ANALYTICAL PROCEDURES

B-1 Alcohol Content of Unleaded Gasoline
B-2 Automatic RVP Instrument Method

APPENDIX B-1
ALCOHOL CONTENT IN UNLEADED GASOLINE

% Methanol, Ethanol, and T-B in Gasoline

Scope

An internal standard, isoproponal, is added in known concentrations, along with a pre-determined volume of gasoline sample, to distilled water. The alcohols present in the gasoline are extracted with the distilled water and the extract introduced into a gas chromatography column. The eluted alcohols are detected by a flame ionization detector and recorded on an integrator. The peak areas are measured and applied to the appropriate calibration curve, from which the volume percent is obtained.

Method

1. Insert the column for alcohols in side "A" or of G.C. - Column-SS Porapak QS 80-100 mesh.
2. Set instrument on FID.
3. Carrier gas is helium - Auxiliary gases are Hydrogen and air to light the detector.

Conditions

He -	Carrier gas	25 cc/min at 60 psi
	Hydrogen	30 cc/min at 13.5 psi
	Air	250 cc/min at 28 psi

Temperature

Oven 175°C
Injection Port 200°C
Detector 250°C

Integrator

Delay - off
Stop - 5 min.
Area reject - 100 - (10^2)
Chart Speed - 1 cm/min
Slope Sense - 1.00
Attenuation - 64

FID

Range - 10
Single Channel
Atten. set on integrator
Zero - as needed for baseline
A & B side (not Diff.)

Sample Size

0.75µℓ

1. Light detector and wait 15 min for instrument to stabilize. During this period make up standard and extract the sample and standards.

Standard Preparation

Stock Standards - all of the standards must be extracted before being injected.

Std. Conc.	MeOH, ETOH, & T-Butyl
0.0%	--
0.1%	25 µℓ
0.5%	125 µℓ
1.0%	250 µℓ
3.0%	750 µℓ
5.0%	1250µℓ
7.0%	1750µℓ
10.0%	2500µℓ
12.0%	3000µℓ

Dilute to 25 m with Indolene.

Extraction of Alcohol - for Std. & Samples

10 mℓ of D.I. H_2O, along with 5 mℓ of sample or std. and 50 µℓ of Isopropyl alcohol are added to a 1 oz. jar. The mixture is shaken for 10 min. on a mechanical shaker and then let stand for 30 min. to assure separation into layers. Part of the lower water layer is then removed for injection into the G.C.

All standards and samples are run, recording the peak areas for MeOH, ETOH, T-Butyl, and Isopropyl (Int. Std.)

Calculation

Divide the area of the MeOH peak by the area of the Int. Std. to get a ratio. Do this for the other two alcohols. The ratio is the number used for calculating percent alcohol.

Run a linear regression on the standard curve for each of the 3 alcohols. There will be three answers for each sample - % MeOH, % ETOH, and % T-Butyl.

Notes

Do not use acetone to clean the syringe between samples - use the next sample to be injected and rinse the syringe 4-5 times before injecting the sample.

APPENDIX B-2
AUTOMATIC RVP INSTRUMENT METHOD

(Excerpts from the Maintenance and Operating Instructions)

DESCRIPTION

The Reid Vapor Pressure Instrument operates automatically - after sample loading - to determine the Reid Vapor Pressure of gasolines and other hydrocarbons. The instrument reproduces manual ASTM test data.*

CALIBRATION PROCEDURES, FULL RANGE

This instrument measures the vapor pressure in psia of hydrocarbons at 100°F, expanded to five times its liquid volume. An equation relating absolute pressure to Reid Vapor Pressure has been developed by computer analysis of instrument data versus ASTM D-323 data for a large number of hydrocarbon samples. The instrument zero and span controls have been adjusted to convert absolute pressure signals from the pressure transducer to equivalent RVP values for the direct display of RVP on the meter.

OPERATION

Sample handling, including filling the sample cup, follows the ASTM D-323 procedure - except the cup is kept dry. (No water can be permitted in the sample or sample system, and the sample need not be air-saturated).

The cup containing the sample is coupled to the instrument inlet fitting, and a push-button "start" switch is momentarily depressed. The start light will illuminate. At the end of 4 minutes, this light will go out, indicating completion of the analysis. The RVP value for the sample will be locked on the digital panel meter and may be read and recorded anytime before starting the next test.

Depression of the "start" switch provides the impulse to start a 4-minute cycle. The timer operates to produce the required analysis program.

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*ASTM Method D-323, "Test for Reid Vapor Pressure of Petroleum," Part 23 of ASTM Book of Standards.

APPENDIX C

CALCULATION OF VOLATILITY INDICES

C-1 Calculated EI and FEVI Volatility Indices

APPENDIX TABLE C-1. CALCULATED EI AND FEVI VOLATILITY INDICES

Sample Number	RVP, psi	% Evaporated at 100°F	% Evaporated at 200°F	EI	% Evap. at 158°F	FEVI	% by Volume MeOH	% by Volume TBA
1	14.2	9.4	53.3	23.8	40.3	19.4	4.9	4.3
2	14.3	8.9	51.3	23.7	39.2	19.4	4.6	4.2
3	14.1	10.6	49.2	22.5	36.8	18.9	4.6	4.1
4	13.5	11.7	53.5	22.3	40.0	18.7	0	0.3
5	13.5	12.8	50.6	21.4	37.9	18.4	0	0.2
6	13.6	9.6	54.9	23.4	41.1	18.9	0	3.9
7	13.3	10.7	57.5	23.3	42.9	18.9	0	7.0
8	14.1	10.0	53.8	23.6	40.0	19.3	0	4.8
9	13.5	9.3	55.1	23.4	40.4	18.8	0	6.9
10	14.0	11.1	57.9	24.0	43.8	19.7	0	3.9
11	13.6	9.6	54.1	23.2	40.7	18.9	0	4.6
12	13.5	8.1	53.8	23.6	37.8	18.4	0	6.8
13	14.3	11.3	59.4	24.6	45.0	19.4	0	5.9
14	13.4	9.2	55.5	23.5	40.9	18.7	0	7.0
15	13.8	9.7	54.1	23.4	39.5	18.9	0	5.8
16	13.4	8.5	56.1	23.8	42.0	18.9	0	5.8
17	13.5	8.5	55.7	23.8	41.6	18.9	0	5.3
18	13.9	7.5	53.8	24.2	41.2	19.3	0	1.1
19	13.8	9.4	52.1	23.1	39.7	19.0	0	0.8
20	13.4	8.8	57.7	24.0	43.2	19.0	0	6.1
21	13.2	7.3	51.9	23.1	38.2	18.2	4.6	4.0
22	13.7	6.4	51.0	23.7	38.8	18.7	4.5	4.2
23	13.7	6.9	51.4	23.7	37.9	18.6	4.7	4.2
24	13.4	8.8	54.1	23.3	40.0	18.6	0	6.1
25	12.9	5.8	49.4	22.7	35.9	17.6	4.7	4.2
26	13.1	5.8	49.4	22.9	36.2	17.8	4.6	4.0
27	13.1	6.7	51.5	23.1	38.4	18.1	4.7	4.2
28	12.7	3.5	47.9	22.9	34.8	17.2	4.5	4.0
29	13.1	5.9	51.0	23.2	37.8	18.0	4.7	4.2
30	12.7	5.6	48.9	22.4	36.2	17.4	4.5	4.0
31	13.1	5.5	50.3	23.2	37.4	18.0	4.9	4.4
32	13.1	8.8	51.7	22.5	37.8	18.0	3.3	2.9
33	13.2	6.8	50.6	23.0	38.1	18.2	4.6	4.1
34	13.1	9.1	51.9	22.4	38.8	18.1	4.7	4.1
35	12.4	8.6	51.3	21.7	37.8	17.3	4.7	4.1
36	14.3	9.1	51.4	23.9	38.4	19.3	4.7	4.2
37	12.9	5.9	50.0	22.8	36.8	17.7	4.7	4.1
38	12.9	6.8	49.4	22.4	36.1	17.6	4.6	4.1
39	13.1	6.5	50.3	22.9	37.0	17.9	4.5	4.0
40	13.8	7.9	53.4	23.9	40.6	19.1	4.8	4.3

EI = 1.1xRVP - 0.32x(% EVAP @ 100°F) + 0.21x(% EVAP @ 200°F)
FEVI = RVP + 0.13x(% EVAP @ 158°F)